

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

## PCT

To:

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### NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (PCT Rule 71.1)

Date of mailing  
(day/month/year)

07.10.2005

Applicant's or agent's file reference  
246

#### IMPORTANT NOTIFICATION

International application No.  
PCT/EP2004/006238

International filing date (day/month/year)  
08.06.2004

Priority date (day/month/year)  
04.07.2003

Applicant  
UMICORE et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

#### 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:



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# PCT

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 246	<b>FOR FURTHER ACTION</b>		See Form PCT/PEA/416
International application No. PCT/EP2004/006238	International filing date (day/month/year) 08.06.2004	Priority date (day/month/year) 04.07.2003	
International Patent Classification (IPC) or national classification and IPC C22B19/04, C22B19/34, C22B5/10, C22B5/12, C22B5/16, C22B13/02			
Applicant UMICORE et al.			
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau) a total of 4 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>			
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>			
Date of submission of the demand  14.01.2005		Date of completion of this report  07.10.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized Officer  Bjoerk, P  Telephone No. +49 89 2399-8452	



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/006238

**Box No. I Basis of the report**

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

**Description, Pages**

1, 2, 5-8	as originally filed
3, 4	received on 19.01.2005 with letter of 14.01.2005

**Claims, Numbers**

1-13	received on 19.01.2005 with letter of 14.01.2005
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/006238

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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1. Statement

Novelty (N)	Yes: Claims	1-13
	No: Claims	
Inventive step (IS)	Yes: Claims	1-13
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-13
	No: Claims	

2. Citations and explanations (Rule 70.7):

**see separate sheet**

1. The application relates to a process for extracting metal values from Zn-, Fe- and Pb-bearing residues and involves (i) a direct reduction step producing a metallic Fe-bearing phase, (ii) an extraction of Zn and Pb from the thus obtained first fumes, (iii) an oxidising smelting step to produce an Fe-bearing slag and (iv) an extraction of metals from the thus obtained second fumes.
2. The originally filed claims have been modified by removing in the last step of claim 1 "and valorising at least part of their metallic contents" and by adding a new, dependent, claim 10 relating to this valorisation. These amendments have a basis in the application as originally filed, in particular on page 3, line 41 to page 4, line 1 of the description and therefor fulfill the requirement of Art.34(2)(b) PCT.
3. Reference is made to the following documents, which are both cited in the application:

D1 = Heard R. et al, "Recycling of Zinc-Bearing Residues with the PRIMUS ® Process", Iron Steelmaker I and SM, Vol.30, Nr 4, April 2003, p.55-60

D2 = Esna-Ashari M and Kerney U, "Smelting Reactor for Recovering Zinc from Industrial Low Zinc Bearing Residues", Erzmetall 53 (2000), Nr 6, p. 373-384

D1 discloses the PRIMUS ® process whereby Zn-bearing residues are submitted to (i) direct reduction in a multiple hearth furnace (Fig.2) to produce a reduced Fe-bearing phase and Zn- and Pb-bearing fumes, (ii) extraction of the Zn- and Pb-bearing fumes for valorisation of Zn and Pb (paragraph bridging pages 58 and 59), (iii) melting of the Fe-bearing phase in an electric furnace, thereby producing both metal melt for the pig iron production and a slag suitable for road or building construction (page 59, middle and right columns) and (iv) extraction of offgases from the melting furnace for collection and cleaning in the primary exhaust line (page 60, left column, 3rd bullet).

D2 discloses a process for extracting metal values from Zn-, Fe- and Pb-bearing residues with the following steps: (i) smelting in a reactor in order to obtain an FeO-bearing phase and Zn- and Pb-fumes, (ii) an extraction of the Zn- and Pb-fumes via a settler placed below the smelting reactor into a waste heat boiler for collection in a bag house, (iii) an oxidising smelting with the help of lances in the settler to produce an Fe-bearing slag and (iv) an additional dezincing and deleading from further fumes originating in step (iii) (see "1. Process description" on pages 374-375 and Fig.1).

3. The process of present claim 1 differs from the PRIMUS® process of D1 through the step (iii) of an oxidising smelting step to produce an Fe-bearing slag. In D1, the reduced iron is intended for pig iron production and not for its recovery in a slag phase.

The process also differs from that of D2 in that the step (i) is that of a direct reduction to produce metallic Fe-bearing phase. In D2 the smelting does not lead to a metallic Fe-bearing phase.

The subject matter of claim 1 and consequently of its dependent claims 2 to 13 therefore fulfills the requirement of novelty of Art.33(2) PCT.

4. The combination of the processes of D1 and D2 in order to obtain that of present claim 1 is not seen as obvious as these processes lead to different products.

Consequently, the subject matter of claims 1 to 13 is also seen to fulfill the requirement of inventive step of Art.33(3) PCT.

*Amended c. sec 63 3 and 4 +  
claims*

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- The primary aim of the invention is to provide for a process for the separation and recovery of a wide range of non-ferrous metals like Cu, Ag, Ge and Zn from residues of the Zn manufacturing industry; moreover, the process must ensure an environmentally acceptable
- 5 output for Fe. The actual valorisation of Fe is however unimportant due to its relatively low concentration in the contemplated residues and to its rather low intrinsic value. These aims are achieved by a process for the valorisation of metal values in a Zn-, Fe- and Pb-bearing residue, comprising the steps of:
- 10 - subjecting the residue to a direct reduction step, thereby producing a metallic Fe-bearing phase and Zn- and Pb-bearing first fumes;
- extracting the Zn- and Pb-bearing first fumes and valorising Zn and Pb;
- 15 - subjecting the metallic Fe-bearing phase to an oxidising smelting step, thereby producing an Fe-bearing slag and second metals-bearing fumes;
- extracting the second metals-bearing fumes.
- 20 In one embodiment of the invention, in the direct reduction step, a metallic Fe-bearing phase containing at least 50%, and preferably at least 90% of the Fe contained in the Zn-, Fe- and Pb-bearing residue is obtained; in another embodiment, during the oxidising step, Fe in the metallic Fe-bearing phase is oxidised to mainly FeO in the slag,
- 25 and preferably at least 50%, or even at least 90% of the Fe in the metallic Fe-bearing phase is oxidised to FeO.

The Zn-, Fe- and Pb-bearing residue may be a neutral leach residue or a weak acid leach residue. The fluidity of the slag can be enhanced

30 by avoiding massive formation of  $Fe_2O_3$ , thus limiting the oxidation to the formation of mainly FeO. The presence of suitable amounts of an acidic flux such as sand and preferably, of a mixture of an acidic and a basic flux such as lime, limestone or dolomite, also enhances the slag fluidity, thus allowing for a lower working temperature.

35 If present, the major part of the Cu and Ag from the metallic Fe-bearing phase may be collected in a separate Cu-bearing phase during the oxidising smelting step.

40 If the Zn-, Fe- and Pb-bearing residue also contains Ge, the fraction of the Ge present in the first fumes, produced in the direct reduction step, may be separated and forwarded to the oxidising smelting step. This separation of Ge is preferably performed by co-

precipitation with Fe hydroxide or by addition of tannic acid. The same principles apply for In.

The first fumes may advantageously be oxidised in the reactor used for the direct reduction step.

- 5 Also, if the Zn-, Fe- and Pb-bearing residue also contains Ge, at least part of the metallic content of the extracted second metals-bearing fumes can be valorised.

- 10 The reactor used for the direct reduction step can be a multiple hearth furnace; the reactor for the oxidising smelting step can be a submerged lance furnace.

- 15 The details of the invention are now discussed. The first step consists of the reduction of the residue, after addition of reductants such as natural gas, coal or cokes, and possibly fluxes such as limestone ( $\text{CaCO}_3$ ) to avoid sintering of the load, thereby producing Zn- and Pb-bearing fumes and a DRI-bearing phase containing, besides Fe, valuable metals such as Cu and Ag. Through leaching of these fumes, Zn and Pb can be separated in a Pb-  
20 containing residue and a Zn-containing leaching liquor. Ge, if present, is also dissolved in the leaching liquor, and can be precipitated as a Ge-containing residue and fed to the oxidising furnace, further enhancing the global Ge-recovery.

- 25 The DRI-bearing phase is smelted and oxidised in a second furnace, preferably after addition of limestone and sand. The oxidation of Fe to  $\text{FeO}$ , and possibly to  $\text{Fe}_2\text{O}_3$ , is particularly exothermic and brings in all the needed enthalpy. The process remains autogenous, even when e.g. 10% of the total feed consists of Ge-containing residues with  
30 moisture content of around 25%. However, if more than 50% of the Fe is oxidised to  $\text{Fe}_2\text{O}_3$ , instead of to  $\text{FeO}$ , the rise in liquidus temperature of the slag entails disadvantages such as increased lining wear and higher energy demands. The fact that Fe is slagged instead of being recovered as a metal, is a small price to pay for  
35 achieving an excellent separation and recovery of the non-ferrous metals. The slag appears to be environmentally acceptable and can even be upgraded as gravel substitute in concrete. Next to this slag, two other streams can be recovered in this operation: fumes, typically containing Ge and In, and a Cu-bearing phase containing  
40 precious metals such as Ag. This phase can be refined in a classical Cu or precious metals flowsheet, separating the Cu and Ag in a Cu-rich and a Ag-rich stream. The fumes can be leached and used as feedstock for the production of Ge.



CLAIMS

1. Process for the valorisation of metal values in a Zn-, Fe- and Pb-bearing residue, comprising the steps of:
- subjecting the residue to a direct reduction step, thereby producing a metallic Fe-bearing phase and Zn- and Pb-bearing first fumes;
  - extracting the Zn- and Pb-bearing first fumes and valorising Zn and Pb;
  - subjecting the metallic Fe-bearing phase to an oxidising smelting step, thereby producing an Fe-bearing slag and second metals-bearing fumes;
  - extracting the second metals-bearing fumes.
2. Process according to claim 1, whereby in the direct reduction step, a metallic Fe-bearing phase containing at least 50%, and preferably at least 90% of the Fe contained in the Zn-, Fe- and Pb-bearing residue is obtained.
3. Process according to claims 1 or 2, characterised in that during the oxidising step, Fe in the metallic Fe-bearing phase is oxidised to mainly FeO in the slag.
4. Process according to claim 3, whereby in the oxidising smelting step, at least 50%, and preferably at least 90% of the Fe in the metallic Fe-bearing phase is oxidised to FeO.
5. Process according to any one of claims 1 to 4, wherein the Zn-, Fe- and Pb-bearing residue is a neutral leach residue or a weak acid leach residue.
6. Process according to claims 3 or 4, characterised in that an acidic flux and preferably, a mixture of an acidic and a basic flux are present in the oxidising smelting step.
7. Process according to any one of claims 1 to 6, characterised in that the Zn-, Fe- and Pb-bearing residue contains Cu and Ag, and that, during the oxidising smelting step, a separate Cu-alloy phase is produced containing a major part of the Cu and Ag.
8. Process according to any one of claims 1 to 7, characterised in that the Zn-, Fe- and Pb-bearing residue contains Ge, and that, after

the direct reduction step, the fraction of the Ge present in the first fumes is separated and forwarded to the oxidising smelting step.

- 5 9. Process according to claim 8, whereby the separation of Ge is performed by co-precipitation with Fe hydroxide or by addition of tannic acid.
- 10 10. Process according to any one of claims 1 to 7, characterised in that the Zn-, Fe- and Pb-bearing residue contains Ge, and that, after extracting the second metals-bearing fumes, at least part of their metallic content is valorised.
- 15 11. Process according to any one of claims 1 to 10, whereby the first fumes are oxidised in the reactor used for the direct reduction step.
12. Process according to any one of claims 1 to 11, whereby the reactor used for the direct reduction step is a multiple hearth furnace.
- 20 13. Process according to any one of claims 1 to 12, whereby the reactor used for the oxidising smelting step is a submerged lance furnace.